US009230821B2

(12) **United States Patent**
Hibino et al.

(10) **Patent No.: US 9,230,821 B2**
(45) **Date of Patent: Jan. 5, 2016**

(54) **DRY ETCHING AGENT AND DRY ETCHING METHOD USING THE SAME**

(71) Applicant: **Central Glass Company, Limited**, Ube-shi, Yamaguchi (JP)

(72) Inventors: **Yasuo Hibino**, Shiki (JP); **Tomonori Umezaki**, Ube (JP); **Akiou Kikuchi**, Ube (JP); **Isamu Mori**, Tokyo (JP); **Satoru Okamoto**, Fujimino (JP)

(73) Assignee: **Central Glass Company, Limited**, Ube-shi (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/271,647**

(22) Filed: **May 7, 2014**

(65) **Prior Publication Data**

US 2014/0242803 A1 Aug. 28, 2014

Related U.S. Application Data

(62) Division of application No. 13/576,093, filed as application No. PCT/JP2011/051304 on Jan. 25, 2011.

(30) **Foreign Application Priority Data**

Feb. 1, 2010 (JP) 2010-020294
Feb. 1, 2010 (JP) 2010-020295
Jan. 21, 2011 (JP) 2011-011049
Jan. 21, 2011 (JP) 2011-011050

(51) **Int. Cl.**
H01L 21/302 (2006.01)
H01L 21/461 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC ***H01L 21/31055*** (2013.01); ***C09K 13/00*** (2013.01); ***H01L 21/3065*** (2013.01); ***H01L 21/31116*** (2013.01); ***H01L 21/32136*** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

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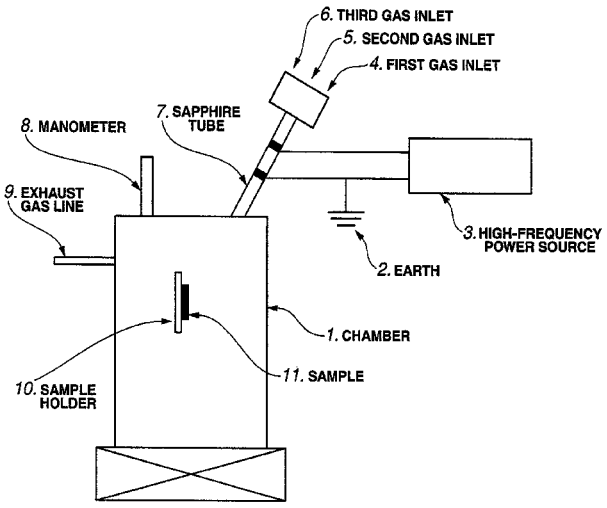
Primary Examiner — Stephanie Duclair
(74) *Attorney, Agent, or Firm* — Crowell & Moring LLP

(57) **ABSTRACT**

A dry etching agent according to the present invention contains (A) a fluorinated propyne represented by the chemical formula: $CF_3C{\equiv}CX$ where X is H, F, Cl, Br, I, CH_3, CFH_2 or CF_2H; and either of: (B) at least one kind of gas selected from the group consisting of O_2, O_3, CO, CO_2, $COCl_2$ and COF_2; (C) at least one kind of gas selected from the group consisting of F_2, NF_3, Cl_2, Br_2, I_2 and YFn where Y is Cl, Br or I; and n is an integer of 1 to 5; and (D) at least one kind of gas selected from the group consisting of CF_4, CHF_3, C_2F_6, C_2F_5H, $C_2F_4H_2$, C_3F_8, $C_3F_4H_2$, C_3ClF_3H and C_4F_8. This dry etching agent has a small environmental load and a wide process window and can be applied for high-aspect-ratio processing without special operations such as substrate excitation.

11 Claims, 1 Drawing Sheet



(51) **Int. Cl.**

B44C 1/22	(2006.01)
C03C 15/00	(2006.01)
C03C 25/68	(2006.01)
C23F 1/00	(2006.01)
H01L 21/3105	(2006.01)
H01L 21/3065	(2006.01)
H01L 21/3213	(2006.01)
C09K 13/00	(2006.01)
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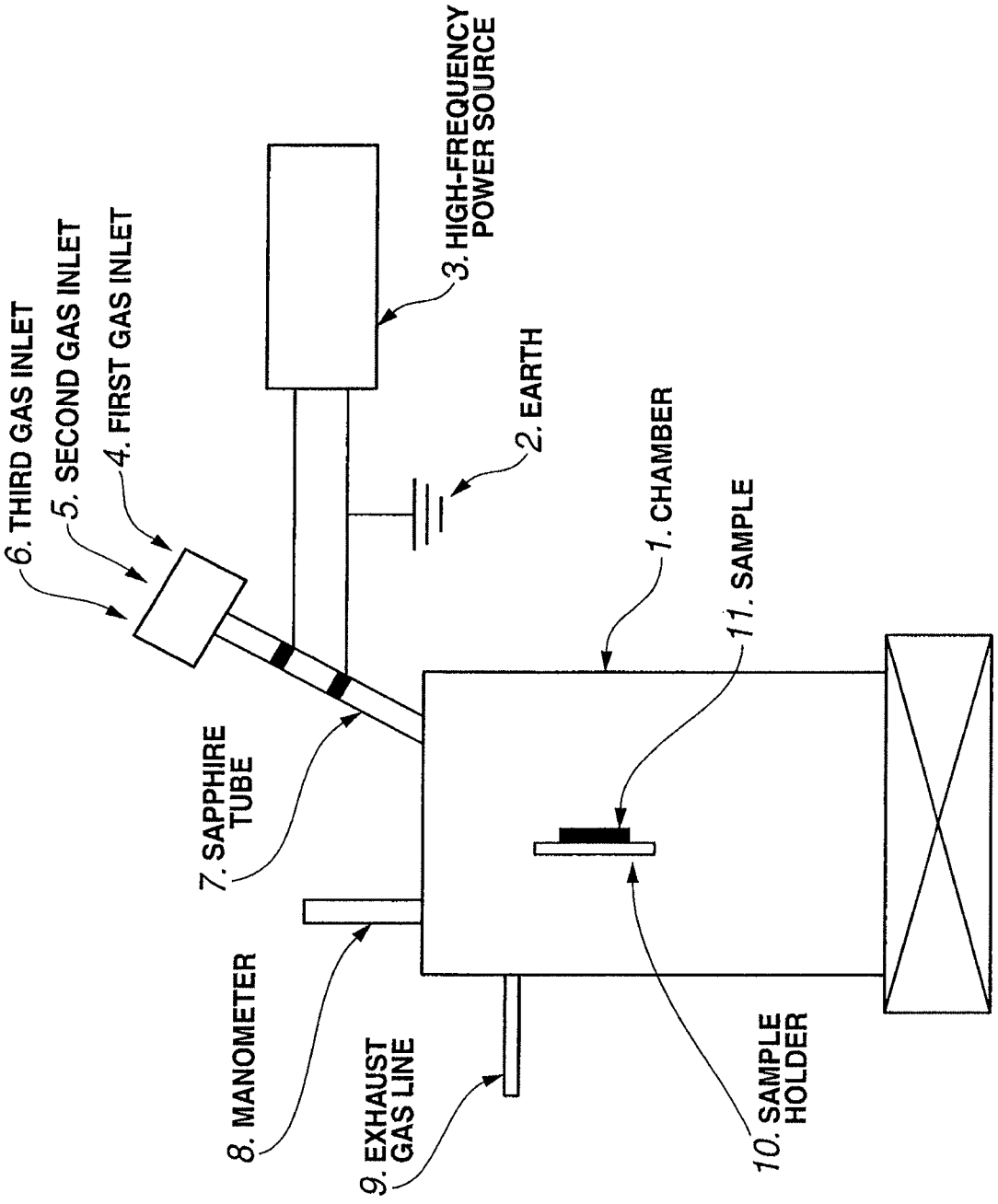
6. THIRD GAS INLET
5. SECOND GAS INLET
4. FIRST GAS INLET
3. HIGH-FREQUENCY POWER SOURCE
2. EARTH
1. CHAMBER
11. SAMPLE
7. SAPPHIRE TUBE
8. MANOMETER
9. EXHAUST GAS LINE
10. SAMPLE HOLDER

DRY ETCHING AGENT AND DRY ETCHING METHOD USING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. application Ser. No. 13/576,093, which is a National Stage of International Application PCT/JP2011/051304, filed Jan. 25, 2011, which claims priority from Japanese Patent Application Nos. 2010-020294 and 2010-020295, filed on Feb. 1, 2010, and Japanese Patent Application Nos. 2011-011049 and 2011-011050, filed on Jan. 21, 2011. The disclosures of the above-identified applications are incorporated by reference herein.

TECHNICAL FIELD

The present invention relates to the use of fluorinated propynes and, more particularly, to a dry etching agent and a semiconductor dry etching method using the dry etching agent.

BACKGROUND ART

In these days, ultra-fine processing techniques are required for production of semiconductor devices. Under such circumstances, dry etching processes are becoming the mainstream in place of wet processes. The dry etching process is a technique in which a fine pattern is formed on a molecule-by-molecule basis on a material surface by generation of a plasma in the vacuum.

For the etching of semiconductor material such as silicon dioxide (SiO_2), perfluorocarbons (PFC) such as CF_4, CHF_3, C_2F_6, C_3F_8 and C_4F_8 and hydrofluorocarbons (HFC) have been used as etching agents in order to increase the etching rate of SiO_2 relative to substrate material such as silicon, polysilicon or silicon nitride. However, the PFC and HFC gases are specified as emission control materials in the Kyoto protocol (COP3) because each of these PFC and HFC gases has a long atmospheric lifetime and a high global warming potential (GWP). There has been a demand for alternative low-GWP materials having high cost efficiency and capable of fine processing in the semiconductor industry.

Patent Document 1 discloses a method using a reactive gas containing a C_4-C_7 perfluoroketone as a cleaning gas or an etching gas. The disclosed reactive gas is not, however, always suitable as the etching gas due to the fact that a decomposition product of the perfluoroketone contains a high-GWP compound and a relatively high-boiling material.

Patent Document 2 discloses a method using a C_2-C_6 hydrofluoro ether (HFE) as a dry etching gas.

Against the above background, it has been demanded to develop compounds having lower GWP and easy to produce industrially. The application of an unsaturated fluorocarbon, which has a double or triple bond in the molecule, for etching process has been examined. As a technique relevant to such an application, Patent Document 3 discloses a method of etching a Si film, a SiO_2 film, a Si_3N_4 film or a high-melting metal silicide with the use of an ether such as $C_aF_{2a+1}OCF{=}CF_2$ or fluorinated olefin such as $CF_3CF{=}CFH$, $CH_3CH{=}CH_2$ etc.

Patent Document 4 discloses a plasma etching method using hexafluoro-2-butyne, hexafluoro-1,3-butadiene, hexafluoropropene or the like as an etching gas.

Patent Document 5 discloses a method of etching an oxide layer on a non-oxide layer e.g. nitride layer with the use of a mixed gas containing: (a) an unsaturated fluorocarbon selected from the group consisting of hexafluorobutadiene, octafluoropentadiene, pentafluoropropene and trifluoropropyne; (b) a hydrofluoro methane selected from the group consisting of monofluoromethane and difluoromethane; and (c) an inert carrier gas.

Patent Document 6 discloses a method using a C_5-C_6 acyclic perfluoroalkyne as a plasma reaction gas.

PRIOR ART DOCUMENTS

Patent Documents

Patent Document 1: Japanese Translation of PCT Application No. 2004-536448

Patent Document 2: Japanese Laid-Open Patent Publication No. H10-140151

Patent Document 3: Japanese Laid-Open Patent Publication No. H10-223614

Patent Document 4: Japanese Laid-Open Patent Publication No. H9-191002

Patent Document 5: Japanese Translation of PCT Application No. 2002-530863

Patent Document 6: Japanese Laid-Open Patent Publication No. 2003-282538

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

As mentioned above, the PFC and HFC compounds are specified as emission control materials because of their high GWP. Although the perfluoroketones, hydrofluoro ethers and hydrofluoro vinyl ethers are known as alternative materials, these alternative materials have the problems that: some little amount of high-GWP PFC compound is contained in the decomposition product; and the alternative material is not easy to produce and is not economical. There has thus been a demand to develop a dry etching agent having not only less effect on the global environment but also performance required. It is further preferable that, in dry etching process where fine processing is required, the etching agent has directivity in anisotropic etching rather than in isotropic etching although SiO_2 undergoes isotropic etching by e.g. F radicals generated from CF_4 gas in plasma etching process. It is also desired that the dry etching agent has less effect on the global environment and high cost efficiency.

The process using the conventional etching gas has a narrow process window as it is necessary to adopt complicated process steps and equipment, limited temperature conditions and operations such as application of vibrations to the gas or substrate as disclosed in Patent Document 5.

It is therefore an object of the present invention to provide a dry etching agent capable of offering a wide process window and forming a good processing shape with no need to use special equipment by control of gas molecular structure and gas composition. It is also an object of the present invention to provide a dry etching method using the dry etching agent.

Means for Solving the Problems

As a result of extensive researches, the present inventors have found an alternative material that is suitable for anisotropic dry etching and has less effect on the global environment. More specifically, the present inventors have found that it is possible to obtain a good processing shape with the use of a mixed gas containing a fluorinated propyne $CF_3C{\equiv}CX$ (where X is H, F, Cl, Br, I, CH_3, CFH_2 or CF_2H) and either an oxygen-containing gas such as O_2, O_3, CO, CO_2, $COCl_2$ or

COF_2, a halogen gas or a halogen compound gas, with or without an inert gas such as N_2, He or Ar, as a dry etching agent.

In other words, the present invention includes the following inventive aspects.

[Inventive Aspect 1]

A dry etching agent, comprising:

(A) a fluorinated propyne represented by the chemical formula: $CF_3C{\equiv}CX$ where X is H, F, Cl, Br, I, CH_3, CFH_2 or CF_2H; and

either of: (B) at least one kind of gas selected from the group consisting of O_2, O_3, CO, CO_2, $COCl_2$ and COF_2; (C) at least one kind of gas selected from the group consisting of F_2, NF_3, Cl_2, Br_2, I_2 and YFn where Y is Cl, Br or I; and n is an integer of 1 to 5; and (D) at least one kind of gas selected from the group consisting of CF_4, CHF_3, C_2F_6, C_2F_5H, $C_2F_4H_2$, C_3F_8, $C_3F_4H_2$, C_3ClF_3H and C_4F_8.

[Inventive Aspect 2]

The dry etching agent according to Inventive Aspect 1, wherein the fluorinated propyne is either 3,3,3-trifluoropropyne ($CF_3C{\equiv}CH$), 1-fluoro-3,3,3-trifluoropropyne ($CF_3C{\equiv}CF$), 1-chloro-3,3,3-trifluoropropyne ($CF_3C{\equiv}CCl$) or 1-bromo-3,3,3-trifluoropropyne ($CF_3C{\equiv}CBr$).

[Inventive Aspect 3]

The dry etching agent according to Inventive Aspect 2, wherein the fluorinated propyne is 3,3,3-trifluoropropyne.

[Inventive Aspect 4]

The dry etching agent according to any one of Inventive Aspects 1 to 3, further comprising at least one kind of gas selected from the group consisting of N_2, He, Ar, Ne and Kr as an inert gas carrier.

[Inventive Aspect 5]

The dry etching agent according to any one of Inventive Aspects 1 to 4, wherein the fluorinated propyne is contained in an amount of 5 to 95 volume %.

[Inventive Aspect 6]

A dry etching method, comprising:

generating a plasma gas from the dry etching agent according to any one of Inventive Aspects 1 to 5; and

selectively etching at least one kind of silicon material selected from the group consisting of silicon dioxide, silicon nitride and silicon carbide by the generated plasma gas.

[Inventive Aspect 7]

The dry etching method according to Inventive Aspect 6, wherein the dry etching agent contains: (A) $CF_3C{\equiv}CH$; (E) at least one kind of oxidizing gas selected from the group consisting of O_2, CO and COF_2; and Ar; and wherein the ratio of volumetric flow rates of (A) $CF_3C{\equiv}CH$, (E) oxidizing gas and Ar is 5 to 95%:1 to 50%:4 to 94% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

[Inventive Aspect 8]

The dry etching method according to Inventive Aspect 6, wherein the dry etching agent contains (A) $CF_3C{\equiv}CH$, (E) at least one kind of oxidizing gas selected from the group consisting of O_2, CO and COF_2, H_2 and Ar; and wherein the ratio of volumetric flow rates of (A) $CF_3C{\equiv}CH$, (E) oxidizing gas, H_2 and Ar is 5 to 95%:1 to 50%:1 to 50%:3 to 93% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

[Inventive Aspect 9]

The dry etching method according to Inventive Aspect 6, wherein the dry etching agent contains: (A) at least one kind of 1-halogeno-3,3,3-trifluoropropyne selected from the group consisting of $CF_3C{\equiv}CF$, $CF_3C{\equiv}CCl$ and $CF_3C{\equiv}CBr$; (F) at least one additive gas selected from the group consisting of O_2, CO, H_2 and COF_2; and Ar; wherein the ratio of volumetric flow rates of (A) 1-halogeno-3,3,3-trifluoropropyne, (F) additive gas and Ar is 5 to 95%:3 to 50%:2 to 92% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** is a schematic view showing one example of remote plasma device used in Examples.

DETAILED DESCRIPTION OF THE EMBODIMENTS

A dry etching agent according to the present invention will be first described below.

The dry etching agent of the present invention contains a fluorinated propyne represented by the chemical formula: $CF_3C{\equiv}CX$ as an effective component and one kind or two or more kinds of other organic and/or inorganic compounds as an additive gas.

In the present invention, there is no particular limitation on the fluorinated propyne $CF_3C{\equiv}CX$ used as the effective component of the dry etching agent as long as the ratio of the number of fluorine atoms to the number of carbon atoms (F/C ratio) is 1.34 or less. Specific examples of the fluorinated propyne are those where X is H, F, Cl, Br, I, CH_3, CFH_2, CF_2H, $CClH_2$, $CBrH_2$, CCl_2H, CBr_2H, CClFH or CBrFH.

The fluorinated propyne $CF_3C{\equiv}CX$ used as the effective component of the dry etching agent has an unsaturated triple bond in the molecule and thereby shows not only the capability of being decomposed in the air but also a much smaller contribution to the global warming than currently used etching materials such as PFC compounds e.g. CF_4 and CF_3H and HFC compounds. Further, it is expected that the ozone depletion potential of the fluorinated propyne is negligibly small as the fluorinated propyne, even when containing Cl or Br, has a very short atmospheric lifetime. The fluorinated propyne $CF_3C{\equiv}CX$ also has such a molecular structure that the triple bond is bonded by a single bond to trifluoromethyl group (CF_3) so as to generate CF_3^+ ions, which have high etching efficiency, while allowing the triple bond moiety to deposit by polymerization.

In order to prevent non-selective etching of a side wall of a target etching workpiece by polymerization of carbon atoms of the etching agent, it is preferable to control the F/C ratio to be as close as possible to 1.

As 3,3,3-trifluoropropyene containing Cl, Br or I is expected to show an ashing treatment effect, the use of such Cl-, Br- or I-containing 3,3,3-trifluoropropyene enables anisotropic etching by removing a fluorocarbon film deposit from the side wall of the target etching workpiece. An ashing treatment may be performed with the use of an oxidizing gas such as O_2 after the etching.

In consequence, the fluorinated propyne $CF_3C{\equiv}CX$ is preferably either 3,3,3-trifluoropropyene ($CF_3C{\equiv}CH$) corresponding to the case where X is H or 1-halogeno-3,3,3-trifluoropropyene ($CF_3C{\equiv}CF$, $CF_3C{\equiv}CCl$, $CF_3C{\equiv}CBr$) corresponding to the case where X is F, Cl or Br. Among others, particularly preferred is 3,3,3-trifluoropropyene having a small F/C ratio of 1 in the molecule.

The fluorinated propyne $CF_3C{\equiv}CX$ used in the present invention can be produced by any known process as disclosed in, for example, Japanese Laid-Open Patent Publication No. 2008-285471.

The dry etching agent of the present invention can be used under various dry etching conditions. Various additives may

preferably be added in view of the properties, productivity and fine processing accuracy etc. of the target film.

In the present invention, the amount of the fluorinated propyne $CF_3C{\equiv}CX$ contained in the dry etching agent is preferably 5 to 95 volume %. It is particularly preferable that the dry etching agent contains about 20 to 90 volume % of the fluorinated propyne $CF_3C{\equiv}CX$ and about 10 to 80 volume % of the additive gas.

As the additive gas, there can be used an oxidizing gas such as O_2 or F_2 or a reducing gas such as H_2 or CO. (Hereinafter, the additive gas may be specifically referred to as "oxidizing gas", "oxygen-containing gas", "halogen-containing gas" or "reducing gas".)

It is preferable to use the oxidizing gas as the additive gas in order to obtain a higher etching rate for improvement in productivity. Specific examples of the oxidizing gas are: oxygen-containing gases such as O_2, O_3, CO_2, CO, $COCl_2$ and COF_2; and halogen gases such as F_2, NF_3, Cl_2, Br_2, I_2 and YFn (where Y is Cl, Br or I; and n is an integer of 1 to 5). Among others, preferred are O_2, CO, COF_2, F_2, NF_3 and Cl_2. These gases can be used alone or in the form of a mixture of two or more kinds thereof.

The amount of the oxidizing gas added is determined depending on the equipment form and performance e.g. output and the properties of the target film and is generally 1/20 to 10 times, preferably 1/10 to 10 times, the flow rate of the fluorinated propyne $CF_3C{\equiv}CX$. If the amount of the oxidizing gas exceeds the above range, the excellent anisotropic etching properties of the fluorinated propyne $CF_3C{\equiv}CX$ may be impaired.

In particular, the etching rate of metal can be selectively increased by the addition of oxygen. Namely, the addition of oxygen makes it possible to significantly improve the selectivity of the etching rate of metal relative to oxide for selective etching of metal.

In order to decrease the amount of F radicals, which promote isotropic etching, it is effective to add the reducing gas. Specific examples of the reducing gas are CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8, HI, HBr, HCl, CO, NO, NH_3 and H_2.

The amount of the reducing gas added is generally in such a range that the ratio (mole ratio) of the fluorinated propyne $CF_3C{\equiv}CX$ and the reducing gas is 10:1 to 1:5, preferably 5:1 to 1:1. The amount of F radials, which are effective in etching, may significantly decrease to cause a deterioration in productivity if the reducing gas is added excessively. Among the above reducing gases, the addition of H_2 or C_2H_2 leads to a decrease in the etching rate of Si, but no change in the etching rate of SiO_2, so as to obtain improvement in etching selectivity, and thereby enables selective etching of SiO_2 relative to Si substrate.

Although the fluorinated propyne such as trifluoropropyne provides a sufficient etching effect, the other gas such as CF_4, CHF_3, CH_2F_2, CH_3F, C_2F_6, $C_2F_4H_2$, C_2F_5H, $C_3F_4H_2$, C_3F_5H or C_3ClF_3H can be added to the fluorinated propyne in order to promote anisotropic etching.

The amount of the other gas added is generally 10 times or less the flow rate of the fluorinated propyne $CF_3C{\equiv}CX$. If the amount of the other gas is 10 times or more, the excellent etching properties of the fluorinated propyne $CF_3C{\equiv}CX$ may be impaired.

An inert gas such as N_2, He, Ar, Ne or Kr, can be added, together with the oxidizing gas, into the etching agent of the present invention as required. The combined use of the fluorinated propyne $CF_3C{\equiv}CX$ and the inert gas, notably Ar, produce a synergistic effect to obtain a higher etching rate although the inert gas also serves as a diluent gas.

The amount of the inert gas added is determined depending on the equipment form and performance e.g. output and gas discharge rate and the properties of the target film and is preferably 1/10 to 30 times the flow rate of the fluorinated propyne $CF_3C{\equiv}CX$.

The following are preferred composition examples of the dry etching agent of the present invention. In each example, the sum of volume % of gas components is 100%.

In the case of using $CF_3C{\equiv}CH$ and the oxygen- or halogen-containing gas (e.g. O_2, CO, COF_2, F_2, Cl_2), the flow rate ratio of the $CF_3C{\equiv}CH$ and the oxygen- or halogen-containing gas is preferably in the range of 5 to 95%:5 to 95%, more preferably 20 to 80%:20 to 80% in terms of volume %.

In the case of using $CF_3C{\equiv}CH$, the oxygen- or halogen-containing gas (e.g. O_2, CO, COF_2, F_2, Cl_2) and the inert gas (e.g. Ar), the flow rate ratio of the $CF_3C{\equiv}CH$, the oxygen- or halogen-containing gas and the inert gas is preferably in the range of 5 to 95%:1 to 50%:4 to 94%, more preferably 5 to 80%:10 to 40%:10 to 85%, in terms of volume %.

In the case of using $CF_3C{\equiv}CH$, the oxygen- or halogen-containing gas (e.g. O_2, CO, COF_2, F_2, Cl_2) and the reducing gas (e.g. H_2), the flow rate ratio of the $CF_3C{\equiv}CH$, the oxygen- or halogen-containing gas and the reducing gas is preferably in the range of 5 to 95%:1 to 50%:4 to 94%, more preferably 10 to 80%:10 to 40%:10 to 80%, in terms of volume %.

In the case of using $CF_3C{\equiv}CH$, the oxygen- or halogen-containing gas (e.g. O_2, CO, COF_2, F_2, Cl_2), the reducing gas (e.g. H_2) and the inert gas (e.g. Ar), the flow rate ratio of the $CF_3C{\equiv}CH$, the oxygen- or halogen-containing gas, the reducing gas and the inert gas is preferably in the range of 5 to 95%:1 to 50%:1 to 50%:3 to 93%, more preferably 5 to 80%:5 to 40%:5 to 40%:10 to 85%, in terms of volume %.

In the case of using $CF_3C{\equiv}CX$ ($CF_3C{\equiv}CF$, $CF_3C{\equiv}CCl$, $CF_3C{\equiv}CBr$) and the oxidizing or reducing gas (e.g. O_2, CO, COF_2, F_2, Cl_2, H_2), the flow rate ratio of the $CF_3C{\equiv}CX$ and the oxidizing or reducing gas is preferably in the range of 5 to 95%:5 to 95%, more preferably 20 to 80%:20 to 80%, in terms of volume %.

In the case of using $CF_3C{\equiv}CX$ ($CF_3C{\equiv}CF$, $CF_3C{\equiv}CCl$, $CF_3C{\equiv}CBr$), the oxidizing or reducing gas (e.g. O_2, CO, COF_2, F_2, Cl_2, H_2) and the inert gas (e.g. Ar), the volumetric flow rate ratio of the $CF_3C{\equiv}CX$, the oxidizing or reducing gas and the inert gas is preferably in the range of 5 to 95%:3 to 50%:2 to 92%, more preferably 10 to 80%:10 to 40%:10 to 80%.

Next, an etching method using the dry etching agent according to the present invention will be described below.

The dry etching agent of the present invention can be used for various workpieces such as B, P, W, Si, Ti, V, Nb, Ta, Se, Te, Mo, Re, Os, Ru, Ir, Sb, Ge, Au, Ag, As and Cr and compounds thereof, notably oxides, nitrides, carbides, fluorides, oxyfluorides, silicides and alloys thereof, laminated on substrates such as silicon wafer, metal plate, glass, single crystal and polycrystal. In particular, the dry etching agent can be suitably used for semiconductor materials. Specific examples of the semiconductor materials are silicon materials such as silicon, silicon oxide, silicon nitride, silicon carbide, silicon oxyfluoride and silicon oxycarbide, tungsten and rhenium and silicides thereof, titanium, titanium nitride, ruthenium, ruthenium silicide, ruthenium nitride, tantalum, tantalum oxide, oxytantalum fluoride, hafnium, hafnium oxide, oxyhafnium silicide and hafnium zirconium oxide.

In the etching method using the dry etching agent of the present invention, there is no particular limitation on the etching technique and reaction conditions. For example, reac-

tive ion etching (RIE), electron cyclotron resonance (ECR) plasma etching or microwave etching can be adopted as the etching technique.

In the present embodiment, the etching method includes the steps of generating a plasma of the propyne gas from the dry etching agent in the etching equipment and etching a given area of the target workpiece by the generated plasma in the etching equipment. In the case of producing a semiconductor device, for example, it is feasible to form a silicon oxide film or a silicon nitride film on a silicon wafer, apply a resist with specific openings onto the silicon oxide or nitride film, and then, etch the openings in the resist in such a manner as to remove parts of the silicon oxide or nitride film.

In order to perform anisotropic etching, the pressure of the gas during the etching is preferably in the range of 0.133 to 133 Pa. If the gas pressure is lower than 0.133 Pa, the etching rate may be decreased. On the other hand, the selectivity to the resist may be impaired if the gas pressure exceeds 133 Pa.

The volumetric flow rate ratio of the fluorinated propyne $CF_3C{\equiv}CX$, the oxygen-containing gas, reducing gas or halogen-containing gas (e.g. O_2, CO, H_2, COF_2, F_2, Cl_2) and the inert gas (e.g. Ar) during the etching is controlled to within the above-mentioned volume % range.

The flow rate of the gas is determined depending on the reactor capacity of the etching equipment, the wafer size and the like and is preferably in the range of 10 to 10000 SCCM.

The etching temperature is preferably 300° C. or lower. It is particularly preferable that the etching temperature is 240° C. or lower in order to perform anisotropic etching. At high temperatures exceeding 300° C., there is a tendency that isotropic etching takes place so that a desired level of processing accuracy cannot be obtained. Further, the resist is unfavorably significantly etched under such high-temperature conditions.

There is no particular limitation on the etching time. The etching time is generally of the order of 5 to 30 minutes. As the etching time varies depending on the progress of the etching treatment, it is preferable to adjust the etching time as appropriate by monitoring the progress of the etching treatment.

It is feasible to improve the selectivity of the etching rate e.g. between the silicon and the silicon oxide film during contact-hole processing by mixing hydrogen or hydrogen-containing compound gas with the etching gas and/or by adjusting the gas pressure, flow rate and temperature as appropriate.

EXAMPLES

The present invention will be described in more detail below by way of the following examples. It should be noted that the following examples are illustrative and are not intended to limit the present invention thereto.

Examples 1 to 15

Using an experimental device of FIG. **1**, contact-hole processing was carried out with the use of a dry etching gas containing 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$, an additive gas and, optionally, an inert gas.

As shown in FIG. **1**, the experimental device had a chamber **1**, an earth **2**, a high-frequency power source **3** (13.56 MHz, 2.2 W/cm^2), a first gas inlet **4**, a second gas inlet **5**, a third gas inlet **6**, a sapphire tube **7**, a manometer **8** and an exhaust gas line **9**. The 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$, the additive gas and the inert gas were introduced from the first, second and third gas inlets **4**, **5** and **6** into the sapphire tube **7**, respectively. In the sapphire tube **7**, the introduced gas was excited by the high-frequency power source **3** to generate an active species. The generated active species was fed to a sample **11** on a sample holder **10** inside the chamber **1** whereby the sample **11** was subjected to etching. During the etching, the gas pressure inside the chamber **1** was set to 1.33 Pa; and the substrate temperature was set to 200° C. The sample **11** used in each example was that obtained by forming a SiO2 or silicon nitride interlayer dielectric film on a single crystal silicon wafer and applying a resist mask with openings as an etching mask to the SiO_2 or silicon nitride film. After the etching, the sample was evaluated for the processing shape of the vicinity of the resist opening and the selectivity of the etching rate of SiO_2 or silicon nitride film to the resist. The evaluation results are indicated in TABLE 1.

Comparative Examples 1 to 4

Contact-hole processing was carried out in the same manner as in Examples 1 to 15, except for using CF_4, C_4F_6 ($CF_2{=}CF{-}CF{=}CF_2$) and 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$ alone as dry etching agents in Comparative Examples 1 to 3 and using a mixed gas of 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$ and Ar as a dry etching agent in Comparative Example 4. The evaluation results of the processing shape of the vicinity of the resist opening and the selectivity of the etching rate of SiO_2 or silicon nitride film to the resist in each of Comparative Examples 1 to 4 are indicated in TABLE 1.

TABLE 1

	Gas 1	Flow rate of gas 1 SCCM	Gas 2	Flow rate of gas 2 SCCM	Gas 3	Flow rate of gas 3 SCCM
Comparative Example 1	CF_4	20	—	—	—	—
Comparative Example 2	C_4F_6	20	—	—	—	—
Comparative Example 3	$CF_3C{\equiv}CH$	20	—	—	—	—
Comparative Example 4	$CF_3C{\equiv}CH$	20	—	—	Ar	50
Example 1	$CF_3C{\equiv}CH$	20	O_2	50	—	—
Example 2	$CF_3C{\equiv}CH$	20	O_2	50	H_2	5
Example 3	$CF_3C{\equiv}CH$	20	O_2	50	H_2/Ar	5/100
Example 4	$CF_3C{\equiv}CH$	20	O_2	50	Ar	50
Example 5	$CF_3C{\equiv}CH$	20	CO	50	—	—
Example 6	$CF_3C{\equiv}CH$	20	COF_2	50	—	—
Example 7	$CF_3C{\equiv}CH$	20	CF_4	20	—	—
Example 8	$CF_3C{\equiv}CH$	20	CO	50	Ar	50
Example 9	$CF_3C{\equiv}CH$	20	C_2F_6	20	—	—
Example 10	$CF_3C{\equiv}CH$	20	C_4F_8	20	—	—
Example 11	$CF_3C{\equiv}CH$	20	F_2	50	—	—
Example 12	$CF_3C{\equiv}CH$	20	Cl_2	50	—	—
Example 13	$CF_3C{\equiv}CH$	20	NF_3	50	—	—
Example 14	$CF_3C{\equiv}CH$	20	O_2	50	—	—
Example 15	$CF_3C{\equiv}CH$	20	O_2	50	H_2	5

	Etching rate nm/mm	Selectivity to resist	Aspect ratio	Contact hole processing shape
Comparative Example 1	309	4	5	partially shoulder loss and recessed side wall
Comparative Example 2	338	5	6	partially recessed side wall
Comparative Example 3	422	6	6	no shoulder loss, good side wall
Comparative Example 4	427	6	6	no shoulder loss, good side wall
Example 1	533	6	6 or higher	no shoulder loss, good side wall
Example 2	527	7	6 or higher	no shoulder loss,

TABLE 1-continued

				good side wall
Example 3	549	7	6 or higher	no shoulder loss, good side wall
Example 4	531	6	6 or higher	no shoulder loss, good side wall
Example 5	562	6	6 or higher	no shoulder loss, good side wall
Example 6	588	6	6 or higher	no shoulder loss, good side wall
Example 7	538	8	6 or higher	no shoulder loss, good side wall
Example 8	609	7	6 or higher	no shoulder loss, good side wall
Example 9	523	7	6 or higher	no shoulder loss, good side wall
Example 10	548	7	6 or higher	no shoulder loss, good side wall
Example 11	544	7	6 or higher	no shoulder loss, good side wall
Example 12	546	7	6 or higher	no shoulder loss, good side wall
Example 13	571	7	6 or higher	no shoulder loss, good side wall
Example 14	545	7	6 or higher	no shoulder loss, good side wall
Example 15	537	7	6 or higher	no shoulder loss, good side wall

Test samples
Comparative Examples 1-14 and Examples 1-13: SiO_2 interlayer dielectric film
Examples 14-15: silicon nitride interlayer dielectric film

In the case of using the dry etching agents of Comparative Examples 1 to 4, both of the selectivity to the resist and the aspect ratio were low as shown in TABLE 1. Further, partially shoulder losses and recessed side walls were seen in the samples of these comparative examples.

On the other hand, the dry etching agents of Examples 1 to 4, 6 and 11 to 15 in which the oxidizing additive gas was added to the 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$ (the dry etching agent of the present invention) offered a high etching rate, a high selectivity to the resist, a high aspect ratio and good contact hole processing shape in comparison to those of Comparative Examples 1 and 4 in which no oxidizing gas was used.

In the case of using the dry etching agents of Examples 7, 9 and 10 in which CF_4, C_2F_6 or C_4F_8 was added as the additive gas to the 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$ (the dry etching agent of the present invention), the etching rate, the selectivity to the resist and the aspect ratio were practically sufficient. Good contact hole processing shape was obtained in each of these examples.

The dry etching agents of Examples 5 and 8 in which CO and Ar were added as the second and third gas components to the 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$ also offered a high etching rate, a high selectivity to the resist, a high aspect ratio and good contact hole processing shape.

In particular, the selectivity to the resist was favorable in Examples 2, 3 and 15 where H_2 was added to the dry etching agent.

Further, good contact hole processing shape was obtained in Examples 14 and 15 where the interlayer dielectric film was of silicon nitride.

Examples 16 to 29

Contact-hole processing was carried out in the same manner as in Examples 1 to 15, except for using a fluorinated propyne $CF_3C{\equiv}CX$ (X═F, Cl, Br, I, CH_3, CFH_2, CF_2H) in place of the 3,3,3-trifluoropropyne $CF_3C{\equiv}CH$ as the effective component of the dry etching agent. After the etching, the sample was evaluated for the processing shape of the vicinity of the resist opening and the selectivity of the etching rate of SiO_2 or silicon nitride film to the resist. The evaluation results are indicated in TABLE 2.

Comparative Examples 5 to 6

Contact-hole processing was carried out in the same manner as in Examples 16 to 19, except for using CF_4 alone as a dry etching agent in Comparative Example 5 and using a mixed gas of 3,3,3-trifluoropropyne CF_4 and O_2 as a dry etching agent in Comparative Example 4. The evaluation results of the processing shape of the vicinity of the resist opening and the selectivity of the etching rate of SiO_2 or silicon nitride film to the resist in each of Comparative Examples 5 to 6 are indicated in TABLE 2.

TABLE 2

	Gas 1	Flow rate of gas 1 SCCM	Gas 2	Flow rate of gas 2 SCCM	Gas 3	Flow rate of gas 3 SCCM
Comparative Example 5	CF_4	40	—	—	—	—
Comparative Example 6	CF_4	20	O_2	50	—	—
Example 16	$CF_3C{\equiv}CF$	20	CO	50	—	—
Example 17	$CF_3C{\equiv}CCl$	20	CO	50	—	—
Example 18	$CF_3C{\equiv}CBr$	20	CO	50	—	—
Example 19	$CF_3C{\equiv}CF$	20	COF_2	50	—	—
Example 20	$CF_3C{\equiv}CCl$	20	COF_2	50	—	—
Example 21	$CF_3C{\equiv}CBr$	20	COF_2	50	—	—
Example 22	$CF_3C{\equiv}CCl$	20	F_2	50	—	—
Example 23	$CF_3C{\equiv}CCl$	20	Cl_2	50	—	—
Example 24	$CF_3C{\equiv}CCl$	20	CO	50	Ar	50
Example 25	$CF_3C{\equiv}CCl$	20	O_2	50	Ar	50
Example 26	$CF_3C{\equiv}CCl$	20	CF_4	20	—	—
Example 27	$CF_3C{\equiv}CCl$	20	CH_3F	20	—	—
Example 28	$CF_3C{\equiv}CCl$	20	O_2	50	H_2/Ar	5/100
Example 29	$CF_3C{\equiv}CCF_2H$	40	O_2	50	Ar	50

	Etching rate nm/mm	Selectivity to resist	Aspect ratio	Contact hole processing shape
Comparative Example 5	315	4	5	partially shoulder loss and recessed side wall
Comparative Example 6	465	4	5	partially shoulder loss and recessed side wall
Example 16	621	6	6 or higher	no shoulder loss, good side wall
Example 17	603	6	6 or higher	no shoulder loss, good side wall
Example 18	609	6	6 or higher	no shoulder loss, good side wall
Example 19	673	6	6 or higher	no shoulder loss, good side wall
Example 20	664	6	6 or higher	no shoulder loss, good side wall
Example 21	600	7	6 or higher	no shoulder loss, good side wall
Example 22	697	7	6 or higher	no shoulder loss, good side wall
Example 23	673	7	6 or higher	no shoulder loss, good side wall
Example 24	605	8	6 or higher	no shoulder loss, good side wall
Example 25	618	8	6 or higher	no shoulder loss, good side wall
Example 26	522	7	6 or higher	no shoulder loss, good side wall
Example 27	545	7	6 or higher	no shoulder loss, good side wall
Example 28	568	8	6 or higher	no shoulder loss, good side wall

TABLE 2-continued

Example 29	587	7	6 or higher	no shoulder loss, good side wall

Test samples
Comparative Examples 5-6 and Examples 16-28: SiO_2 interlayer dielectric film
Example 19: silicon nitride interlayer dielectric film

As shown in TABLE 2, both of the selectivity to the resist and the aspect ratio were low in the case of using the dry etching agents of Comparative Examples 5 to 6. Further, partially shoulder losses and recessed side walls were seen in the samples of these comparative examples.

On the other hand, the dry etching agents of Examples 19 to 23, 25, 28 and 29 in which the oxidizing additive gas was added to the fluorinated propyne $CF_3C{\equiv}CX$ (the dry etching agent of the present invention) offered a high etching rate, a high selectivity to the resist, a high aspect ratio and good contact hole processing shape.

The dry etching agent of Example 24 in which CO and Ar were added as the second and third gas components to the fluorinated propyne $CF_3C{\equiv}CX$ also offered a high etching rate, a high selectivity to the resist, a high aspect ratio and good contact hole processing shape.

In particular, the selectivity to the resist was favorable in Example 28 where H_2 was added to the dry etching agent.

Further, the etching rate, the selectivity to the resist and the aspect ratio were practically sufficient even in Examples 26 and 27 where CF_4 or CH_3F was added as the additive gas to the dry etching agent. Good contact hole processing shape was also obtained in each of these examples.

As described above, the fluorinated propype $CF_3C{\equiv}CX$ was contained as the effective component in the dry etching agent of the present invention. The fluorinated propype $CF_3C{\equiv}CX$ has one unsaturated triple bond in the molecule and thereby shows not only the capability of being decomposed in the air but also a much smaller contribution to the global warming than currently used etching materials such as PFC compounds e.g. CF_4 and CF_3H and HFC compounds. The use of the fluorinated propyne in the dry etching agent leads to a small load on the environment. Further, the addition of the oxygen- or halogen-containing gas as a second gas and the addition of the inert gas as a third gas allows a significant improvement in process window so as to meet the demand for high-aspect-ratio processing without special operations such as substrate excitation.

Although the present invention has been described with reference to the above embodiments, various modifications and variations of the above embodiments can be made based on the knowledge of those skilled in the art without departing from the scope of the present invention.

The invention claimed is:

1. A dry etching method, comprising:

generating a plasma gas from a dry etching agent; and

selectively etching at least one kind of silicon material selected from the group consisting of silicon dioxide and silicon nitride by the generated plasma gas,

wherein the dry etching agent comprises:

(A) a fluorinated propyne represented by the chemical formula: $CF_3C{\equiv}CX$ where X is H, F, Cl, Br or, I; and

at least one of:

(B) at least one kind of gas selected from the group consisting of O_2, O_3, CO, CO_2, $COCl_2$ and COF_2;

(C) at least one kind of gas selected from the group consisting of F_2, NF_3, Cl_2, Br_2, I_2 and YFn where Y is Cl, Br or I; and n is an integer of 1 to 5; and

(D) at least one kind of gas selected from the group consisting of CF_4, CHF_3, C_2F_6, C_2F_5H, $C_2F_4H_2$, C_3F_8, $C_3F_4H_2$ and C_4F_8.

2. The dry etching method according to claim **1**, wherein the dry etching agent contains:

(A) $CF_3C{\equiv}CH$ and

(E) at least one kind of oxidizing gas selected from the group consisting of O_2, CO and COF_2; and

wherein the ratio of volumetric flow rates of (A) $CF_3C{\equiv}CH$ and (E) oxidizing gas is 5 to 95%:5 to 95% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

3. The dry etching method according to claim **1**, wherein the dry etching agent contains:

(A) $CF_3C{\equiv}CH$,

(E) at least one kind of oxidizing gas selected from the group consisting of O_2, CO and COF_2, and

Ar; and

wherein the ratio of volumetric flow rates of (A) $CF_3C{\equiv}CH$, (E) oxidizing gas, and Ar is 5 to 95%:1 to 50%:4 to 94% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

4. The dry etching method according to claim **1**, wherein the dry etching agent contains:

(A) $CF_3C{\equiv}CH$,

(E) at least one kind of oxidizing gas selected from the group consisting of O_2, CO and COF_2, and

H_2; and

wherein the ratio of volumetric flow rates of (A) $CF_3C{\equiv}CH$, (E) oxidizing gas, and H_2 is 5 to 95%:1 to 50%:4 to 94% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

5. The dry etching method according to claim **1**, wherein the dry etching agent contains:

(A) $CF_3C{\equiv}CH$,

(E) at least one kind of oxidizing gas selected from the group consisting of O_2, CO and COF_2,

H_2, and

Ar; and

wherein the ratio of volumetric flow rates of (A) $CF_3C{\equiv}CH$, (E) oxidizing gas, H_2, and Ar is 5 to 95%:1 to 50%:1 to 50%:3 to 93% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

6. The dry etching method according to claim **1**, wherein the dry etching agent contains:

(A) at least one kind of 1-halogeno-3,3,3-trifluoropropyne selected from the group consisting of $CF_3C{\equiv}CF$, $CF_3C{\equiv}CCl$ and $CF_3C{\equiv}CBr$ and

(F) at least one additive gas selected from the group consisting of O_2, CO, H_2 and COF_2; and

wherein the ratio of volumetric flow rates of (A) 1-halogeno-3,3,3-trifluoropropyne and (F) additive gas is 5 to 95%:5 to 95% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

7. The dry etching method according to claim **1**, wherein the dry etching agent contains:

(A) at least one kind of 1-halogeno-3,3,3-trifluoropropyne selected from the group consisting of $CF_3C{\equiv}CF$, $CF_3C{\equiv}CCl$ and $CF_3C{\equiv}CBr$;

(F) at least one additive gas selected from the group consisting of O_2, CO, H_2 and COF_2; and

Ar; and

wherein the ratio of volumetric flow rates of (A) 1-halogeno-3,3,3-trifluoropropyne, (F) additive gas, and Ar is 5 to 95%:3 to 50%:2 to 92% assuming that the sum of the volumetric flow rates of the respective gas components is 100%.

8. They dry etching method according to claim **1**, wherein the fluorinated propyne is either 3,3,3-trifluoropropyne ($CF_3C{\equiv}CH$), 1-fluoro-3,3,3-trifluoropropyne ($CF_3C{\equiv}CF$), 1-chloro-3,3,3-trifluoropropyne ($CF_3C{\equiv}CCl$) or 1-bromo-3,3,3-trifluoropropyne ($CF_3C{\equiv}CBr$).

9. The dry etching method according to claim **8**, wherein the fluorinated propyne is 3,3,3-trifluoropropyne.

10. The dry etching method according to claim **1**, wherein the dry etching agent further comprises at least one kind of inert gas selected from the group consisting of N_2, He, Ar, Ne and Kr as a gas carrier.

11. The dry etching method according to claim **1**, wherein the fluorinated propyne is contained in an amount of 5 to 95 volume %.

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